COMPLETE SPECIFICATION

Process for the production of Zeolites

We, VEB FARBENFABRIK WOLFEN, of Wolfen, Kreis Bitterfeld, Germany, a Corporation organised under the laws of Eastern Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the production of zeolites with the structure of type X which simultaneously contain sodium and potassium ions and which are hereinafter referred to as " zeolites of the sodium-potassium X type."

The zeolite with which the present invention is concerned is the mixed sodium-potassium form of the already known zeolite X which hitherto could only be produced in the sodium form by a direct synthesis and is designated 13X. Previously, zeolites of the sodium-potassium X type have been produced from zeolite 13X by ion exchange.

As is known, certain zeolites, which possess a rigid three-dimensional anionic lattice permeated by inner crystalline hollow spaces, are characterised as molecular sieves. The critical openings of these hollow spaces have, in one and the same type of crystal, a very uniform size of, for example, 3, 4, 5, 8 or 9 Å. In a hydrated state, these canals are filled with water which, however, can be almost completely removed by heating to 300 to 650° C., without the crystalline lattice undergoing any change.

These zeolites have a great affinity for the adsorption of all molecules which can pass the canals or openings. Due to the uniform pore size, the adsorption takes place very selectively, whereby there is provided a very wide field of application for the separation, purification and drying of gases and liquids.

These zeolites are constructed from alternately arranged SiO₄ and AlO₄ tetrahedra, i.e. in the crystalline lattice of the zeolite, each silicon and aluminium atom is surrounded by four tetrahedrally arranged oxygen atoms. The basic unit of the crystalline skeleton is the cubooctahedron. The excess negative charge of the AlO₄ tetrahedron is compensated by mono-, di- or trivalent cations. These cations can be exchanged for others, whereby the properties of the zeolites, such as pore size and adsorption capacity, can again be modified. The basic formula of these zeolites can be represented as follows:

$$M_{2/n}O . Al_2O_3 . a\ SiO_2 . b\ H_2O$$
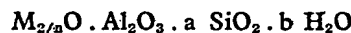
wherein M is a metal of valency n and a and b are numbers.

Many zeolites of this type, such as analcite, chabasite and mordenite, are naturally-occurring. They have been investigated in extensive work by R. M. Barrer. A survey is given in the following paper " Trennung von Molekülen mit Hilfe von Kristallsieben," Brennstoffchemie, 1954, page 325. Because of the very limited extent of their occurrence, the outstanding properties of the zeolite molecular sieves could not be utilised technically so that various types, such as A, X Y and the like, are now produced synthetically (see, for example, British Patent Specifications Nos. 777,232 and 777,233). The finely crystalline powders obtained are, together with binding agents, such as clay, moulded to give granules of the most varied shapes. All these zeolites have a quite specific crystal structure which is independent of the cation. Therefore, the various types of zeolitic molecular sieves can easily be distinguished by their Debye-Scherrer diagrams. The characteristic Debye-Scherrer diagram for zeolites of type X is given in British Patent Specification No. 777,233.

Zeolite sodium-potassium X was previously produced from the sodium form of zeolite X

[Price

by ion exchange. Zeolite 13X was thereby first synthesised by known processes (v. supra). After separating off the zeolite from the mother liquor and washing it out, the filter cake is introduced into a dilute solution of potassium chloride or of potassium hydroxide and stirred for some hours. In order to achieve a sufficiently high degree of exchange, the solution must be replenished several times so that the sodium ions, which unfavourably influence the equilibrium, are removed. Since the selectivity of zeolite X to sodium and potassium ions is of substantially the same size, a considerable excess of potassium must be used. The potassium-enriched zeolite is filtered off, washed and dried. These ion exchange operations are technically time-consuming and laborious. The potassium exchange on zeolite X is not described in detail in the literature. The above description results from our own investigations. Contrary to what is stated in the above-mentioned Patent Specifications, the synthesis of the molecular sieve 13X used as starting material requires a crystallisation time of 40 to 48 hours. Barrer also states that a crystallisation time of 48 hours is necessary for zeolite 13X (J.C.S., 1959, I, 195).

It is known that, depending on the concentration and nature of the starting materials, sodium zeolites, potassium zeolites and mixed sodium-potassium zeolites can be synthesised directly. These types, such as types A, X, Y, R, S, T, W, E, L, D and T, differ from one another in their crystallographic properties, as well as in their adsorption properties (c.f. British Patent Specifications Nos. 777,232; 777,233; 868,846; 905,194; 909,264 and 909,265).

Each of these zeolites is a new type. Hitherto, a synthesis of other cationic forms of these zeolites has always taken place by ion exchange, as in the case of the already-described type sodium-potassium X. However, the production by way of exchange is, as already mentioned above, laborious and necessitates the use of long periods of time. Furthermore,

the crystallisation time of 48 hours for zeolite 13X is, from the technical point of view, very unfavourable.

The problem exists, therefore, of developing a process which enables a zeolite Na—K X to be produced by means of a simple and quick direct process. Such mixed types can have the properties not only of the mixed type but also of the pure sodium form or of the pure potassium form.

According to the present invention, this problem is overcome when, while maintaining a definite concentration ratio, the potassium component is previously added to the reaction mixture in the form of potassium hydroxide, said reaction mixture already containing the sodium ion from the very beginning.

As starting materials there are used the known components: sodium aluminate or aluminium oxides, sodium water glass or silica sol, sodium hydroxide, potassium hydroxide and water.

The mixing of the components takes place at room temperature. The dilute silicate solution is first prepared and the dilute aluminate solution, which also contains the necessary amounts of sodium hydroxide and potassium hydroxide, is allowed to run in, with vigorous stirring. The mixture is homogenised and heated to 50 to 100° C., preferably to 70 to 80° C. During the crystallisation time of at least half an hour, preferably 7 to 10 hours, it is not necessary to stir. No noticeable influence of stirring has been observed. After crystallisation has taken place, the hot reaction mixture is filtered off with suction and washed with water until the pH value of the water running off is between 9 and 11. The molecular sieve obtained is subsequently dried.

The constitution of the reaction mixture lies, expressed in the mol ratio of the oxides, within the following limits, whereby there is no overlap with ranges which are already known. It is important that the zeolite Na—K X is produced with a very low water content of the reaction mixture.

Type	Mol (Na$_2$O + K$_2$O)	Mol Al$_2$O$_3$	Mol SiO$_2$	Mol H$_2$O	$\dfrac{Na_2O}{Na_2O + K_2O}$
Zeolite D	12.6—18.2	1	28	227—820	0.74—0.92
Zeolite E	1.6	1	2	32	0.5
Zeolite L	5.1—14	1	15—28	76.5—714	0—0.74
Zeolite T	5.1—13.2	1	15—30	102—673	0.7—0.8
Zeolite Na-K X produced directly acc. to the present invention	2.0—85	1	0.534—15.7	50—250	0.10—0.90

The sodium-potassium ratio of the reaction mixture used according to the present invention lies within the range:

$$\frac{Na_2O}{Na_2O + K_2O} = 0.10\text{—}0.90$$

The value of x varies, depending on the reaction mixture, between 0.05 and 0.78. The potassium content is always somewhat lower than in the liquid phase.

The lattice plane distances d, obtained

The molecular sieve Na—K X obtained according to the present invention has, in the dehydrated state, the following constitution:

$$(0.98 \pm 0.2)[xK_2O + (1-x)Na_2O] : Al_2O_3 : (2.1 \pm 0.15)SiO_2$$

from Debye-Scherrer plots, are given in the following Table (only the most intensive lines are given); they correspond to the crystal structure of the molecular sieve X:

$$(0.229K_2O + 0.788Na_2O) : Al_2O_3 : 1.977SiO_2$$
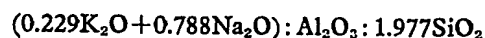
Intensity (estimated)	Lattice plane distance d (Å)
medium	8.75
medium	7.62
medium	5.75
weak	4.84
weak	4.48
strong	3.816
strong	3.362
very weak	3.056
very strong	2.902
medium	2.804
medium	2.673
very weak	2.569
medium	2.422
medium	2.215

As is known for zeolite 13X, the zeolite Na—K X produced according to the present invention also shews at —196° C. a high 5 nitrogen adsorption of 20.5% at a partial pressure of 200 mm.Hg. In contradistinction thereto, the sodium and potassium forms of zeolite A do not shew any nitrogen adsorption at —196° C.; they have narrower pores.

10 Zeolite Na—K X has wide pores, the pore diameters being of from 8—9 Å, rather like zeolite 13X which has pore diameters of 19—25 Å. Therefore, its properties resemble those of zeolite 13 X, especially in the case of 15 low potassium contents.

The production of zeolite Na—K X by the direct synthesis according to the present invention has, in comparison with the known ion exchanger process, the advantage that in 20 the case of the direct synthesis one of the two otherwise necessary and time consuming filtration and washing process is saved, which is of considerable importance in the case of large-scale plant. The technology of the process is simplified and the very laborious ion exchange process is avoided. The capacity of

a plant can thereby be significantly increased.

As already mentioned, the synthesis of zeolite Na—K X according to the present invention has, in comparison with zeolite 13 X, 30 the advantage that the crystallisation time does not amount to 48 hours but is only about 7 hours. From the practical point of view, this is of great importance. This effect is clearly brought about by the presence of the 35 potassium ions. A zeolite which is produced under the same reaction conditions and with the same crystallisation times, without the simultaneous addition of potassium, and which is crystallised from a mixture which 40 only contains sodium ions, exhibits very poor adsorption properties. Furthermore, considerably longer crystallisation times are necessary, i.e. of about 40 to 48 hours.

The zeolite Na—K X produced by the 45 process according to the present invention is superior to all known sodium-potassium zeolites with regard to its adsorption capacity for water, as can be seen from the results set out in the following Table: 50

| Zeolite type	Temperature °C.	pH$_2$O mm. Hg.	g. H$_2$O per 100 g. dry zeolite
Zeolite D	25	1	16.2
Zeolite E	25	1	6.3
Zeolite L	25	4.5	12.6
Zeolite T	25	4.5	16.2
Zeolite Na-K X acc. to present invention	25	0.6	24.5
Zeolite 13X acc. to to our results	25	0.6	24.4

The advantageous use of the process according to the present invention for the production of zeolite Na—K X is clear on the basis of the above-given results; high quality of the zeolite Na—K X with shorter crystallisation times and a technically simpler synthesis. The yields of crystalline material obtained also speak in favour of the synthesis of zeolite Na—K X according to the present invention. When we prepared zeolite 13X using the process described in the literature, 100 g. of zeolite were obtained from 1 litre of reaction mixture whereas, in the case of the production of zeolite Na—K X by the process according to the present invention, 160 g. of zeolite powder were obtained from 1 litre of reaction mixture. The reason for this is that in the case of the synthesis of zeolite Na—K X by the process according to the present invention, the water content of the reaction mixture is much lower than in the case of the synthesis of zeolite 13 X but, nevertheless, an outstanding crystallisation takes place with a crystallisation time of only 7 hours. If, in the case of the synthesis of zeolite 13 X, the water content of the reaction mixture is reduced, then only a poor end product is obtained, even after a crystallisation time of 48 hours.

The following Example is given for the purpose of illustrating the present invention: —

EXAMPLE.

250 ml. concentrated sodium aluminate solution (D^{20}=1.44; aluminium oxide content 18% and sodium oxide content 18.4%) are diluted with 300 ml. water and mixed with 108.5 g. potassium hydroxide and 120 g. sodium hydroxide. This mixture is allowed to run at room temperature, with continuous stirring, into 524 ml. of sodium silicate solution (D^{20}=1.13). After thoroughly homogenising, the reaction mixture is heated to 70—75° C. During the crystallisation time of 7 hours, brief stirring is carried out only at widely spaced intervals of time. The reaction mixture is subsequently filtered with suction, washed with 3600 ml. water and dried. In a dehydrated state, the crystals have the following constitution:

$$(0.229K_2O+0.788Na_2O):Al_2O_3:1.977SiO_2$$
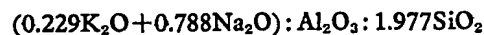
Yield: 195 g.

The water take-up capacity at 25° C. and P_{H_2O} of 0.6 mm. Hg. is 24.6 g. water per 100 g. of dry material.

WHAT WE CLAIM IS: —

1. Process for the production of crystalline zeolitic molecular sieves with the structure of the X type which, in the dehydrated state, have the constitution: —

$$(0.98\pm0.2)[x\ K_2O+(1-x)Na_2O]:Al_2O_3:(2.1\pm0.15)SiO_2$$

in which x has a value between 0.05 and 0.78, by a hydrothermal synthesis, wherein a water-containing sodium-potassium alumino-silicate mixture with the constitution, expressed in terms of mol ratios of oxides:

$$Na_2O+K_2O/Al_2O_3 \quad =2.0\text{---}85$$
$$SiO_2/Al_2O_3 \quad =0.534\text{---}15.7$$
$$H_2O/Al_2O_3 \quad =50\text{---}250$$
$$Na_2O/Na_2O+K_2O \quad =0.10\text{---}0.90$$

5 which has been produced by mixing sodium aluminate or an aluminium oxide, sodium waterglass or silica sol, sodium hydroxide, potassium hydroxide and water, is subjected to a hydrothermal treatment at a temperature 10 of 50—100° C. for at least half an hour.

2. Process according to claim 1, wherein the hydrothermal treatment is carried out at a temperature of 70—80° C.

3. Process according to claim 1 or 2, 15 wherein the hydrothermal treatment is carried out for 7—10 hours.

4. Process according to any of the pre-ceding claims, wherein the reaction mixture is filtered and the molecular sieve obtained washed with water until the water running 25 off has a pH value between 9 and 11, and then dried.

5. Process according to claim 1 for the production of crystalline zeolitic molecular sieves, substantially as hereinbefore described 25 and exemplified.

6. Crystalline zeolitic molecular sieves, whenever produced by the process according to any of claims 1 to 5.